

# REPORT DOCUMENTATION PAGE

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14. ABSTRACT Initially, we developed an ion spectrometer that could be used to study the spectroscopy and reactivity of small ions. For this purpose we characterized the discharge source, forming ions by combining an electrical discharge with a supersonic expansion from a pulsed nozzle. After expanding into a vacuum chamber, the ions were detected using cavity ring-down spectroscopy (CRDS), allowing the population of individual states to be determined on an absolute basis. The CRDS detection of the ions from this source was tested with $N_2^+$ by probing the $B^2E^+ - X^2E^+$ electronic band system. We are also using Hadamard transform time-of-flight mass spectrometry as the basis for producing an instrument that could be used to analyze and identify the components of potentially contaminated samples.						
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## **FINAL PERFORMANCE REPORT**

**TITLE:** Study of Ionic Structure and Ion Reaction  
Dynamics by Cavity Ring-Down Spectroscopy

**GRANT NUMBER:** F49620-01-1-0019

**PRINCIPAL INVESTIGATOR:** Richard N. Zare  
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In Natural Science  
Department of Chemistry

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Stanford, CA 94305-5080

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## **1. OBJECTIVES:**

Initially, the objective of our work was the development of an ion spectrometer, which could be used to study the spectroscopy and reactivity of small ions. For this purpose we planned to characterize the discharge source. In this apparatus, ions are formed by combining an electrical discharge with a supersonic expansion from a pulsed nozzle. After expanding into the vacuum chamber, the ions would be detected using cavity ring-down spectroscopy (CRDS), allowing the population of individual states to be determined on an absolute basis. The number density ( $N$ ) of ions approximately 1 cm from the discharge region is about  $10^8 \text{ cm}^{-3}$ .

During the second year of the grant we added a second objective to our research plan, that of using Hadamard transform time-of-flight mass spectrometry (HT-TOFMS) as the basis for producing an instrument that could be used by technicians in the laboratory or in the field to analyze and identify the components of potentially contaminated samples (solid, liquid, or gas) and for continuous monitoring of air and water quality. The instrument would include interchangeable ion sources (electrospray ionization and gas sampling glow discharge source) and smart software capable of identifying targeted biological and chemical agents, i.e., anthrax, smallpox, Tabun, VX, and transuranium nuclides.

## **2. STATUS OF EFFORT:**

### **A. CRDS of Ions**

The main difficulty in the study of ion-molecular reactions lies in the maintenance of a high ion density. Recently, there have a number of reports on ion generation with an electric discharge. In spite of high yields, ions from a discharge source usually have extremely high rotational and vibrational temperatures, imposing complications on spectroscopic detection. However, it is reported that the temperature could be lowered substantially if the discharge is combined with a supersonic expansion from a nozzle. In our laboratory, a new apparatus was constructed from existing equipment to accommodate such a discharge nozzle. It was found that ions with a number density of  $10^{14} \text{ cm}^{-3}$  could be generated using this instrument.

The cavity ring-down detection of the ions from this source was tested with N<sub>2</sub><sup>+</sup> by probing the N<sub>2</sub><sup>+</sup>B<sup>2Σ<sub>u</sub><sup>+</sup> - X<sup>2Σ<sub>g</sub><sup>+</sup> electronic band system.. A cavity ring-down spectrum could be obtained with a signal-to-noise ratio greater than 100:1.</sup></sup>

## B. HT-TOFMS

By far the simplest and least expensive form of mass spectrometry (MS) is time-of-flight (TOF). In TOFMS, the ion source is pulsed to create packets of ions. In the conventional procedure, the system waits for all the ions in a packet to reach the detector before injecting the next packet of ions. Because of the system delay between packet extractions, orthogonal extraction instruments usually detect between only 5 and 15 percent of the ions in the ion beam. This figure of merit, termed the duty cycle, means that up to 95 percent of the information contained in the ion stream is lost. In contrast, our laboratory has developed an on-line modulation-demodulation scheme that allows, on average, half the ions in the ion stream to strike the ion detector. Moreover, because we modulate the ion beam at a frequency of 10 to 20 MHz, mass spectra can be collected at extraordinarily high rates. As a result, TOFMS performed in this manner can accurately detect rapid, subtle changes in the profile of a sample. Because the modulation scheme is based on a fast Hadamard transform (HT), the technique has been named HT-TOFMS.

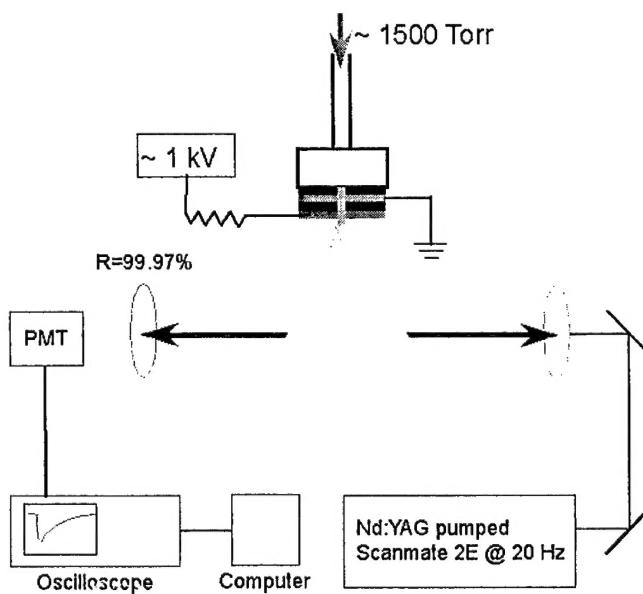
The initial stages of this project focused on proof of principle. Brock, Rodriguez, and Zare published two comprehensive papers that demonstrated the feasibility of the technique and discussed the relevant theory and instrumentation<sup>1,2</sup>. Work since that time has focused on improving figures of merit and application of the technique to relevant problems in analytical chemistry. Future plans involve making the modulation electronics robust and reliable.

1. Brock, A.; Rodriguez, N.; Zare, R. N. *Anal. Chem.* 1998, **70**, 3735-3741.
2. Brock, A.; Rodriguez, N.; Zare, R. N. *Rev. Sci. Instrum.* 2000, **71**, 1306-1318.

### 3. Accomplishments/New Findings:

#### A. CRDS of Ions

The schematics of the instrument are given in Figure 1. Discharge electrodes are attached on top of a pulse nozzle. Electrical shielding from the nozzle body is achieved by inserting a delrin insulator plate between the nozzle and the electrodes.



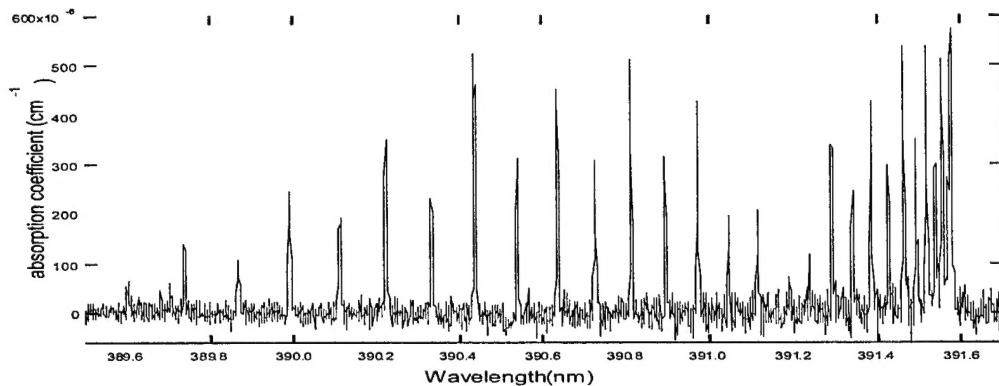
The electrode closer to the nozzle body is electrically grounded while the one further downstream from the nozzle is attached to a negative high voltage supply through an adjustable ballast resistor. This configuration of voltages on the electrodes allows the electron flow to be in the opposite direction of the gas flow, which increases the discharge efficiency.

The voltage and the ballast resistance are tuned to obtain the most stable discharge.

The discharge starts and ceases automatically with gas flow through the aperture. Unlike previous reports, there has been no arcing to the grounded chamber walls. Typically, the discharge occurs with a 400 V difference between the electrodes with about 2 A of current.

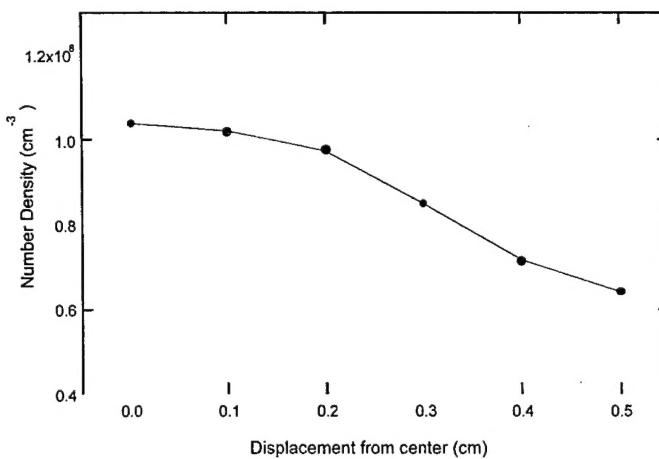
The CRDS axis is set up perpendicular to the gas expansion axis using two high reflectivity mirrors ( $R = 0.9997$  at 390 nm). The light source is the frequency-doubled

output of a dye laser (Scanmate 2E, Lambda Physik) operating with LDS 765 dye pumped by the second harmonic of an Nd:YAG laser (Quantaray). The CRDS spectrum of  $\text{N}_2^+$  thus obtained is illustrated in Figure 2. The line of sight lies 1 cm away from the electrode assembly, leading to the reduction in ion concentration by a factor of about 100 compared to the concentration at the expansion orifice.



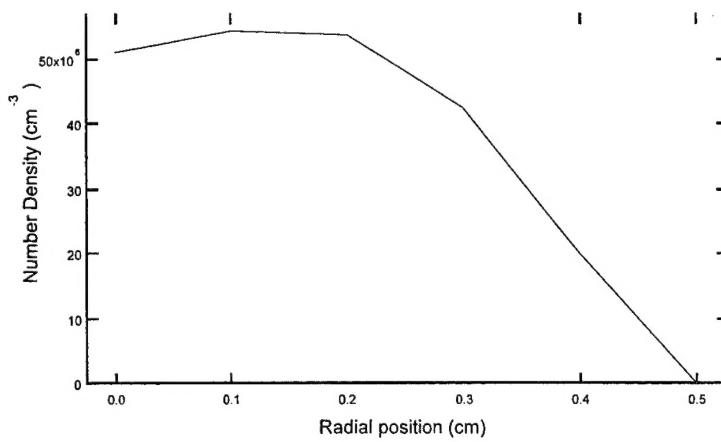
**Figure 2.**  $\text{N}_2^+$  spectrum  $X^2\Sigma_g^+ \leftarrow B^2\Sigma_u^+$

In order to characterize the discharge source, both the spatial and temporal profiles of the discharge were measured. Figure 3 shows the lateral spatial profile for the total number density of  $\text{N}_2^+$ .



**Figure 3. Lateral profile of the discharge source.**

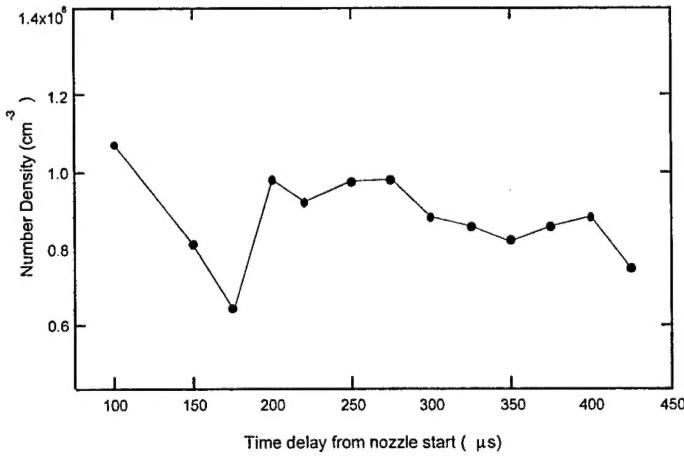
The data in the figure was obtained by recording spectra of slices approximately 1 mm wide separated by approximately 1 cm. The optical axis remained stationary while the discharge nozzle was translated perpendicularly. The figure shows that the number density peaks at the center slice ( $N \sim 1 \times 10^8 \text{ cm}^{-3}$ ) and falls as the discharge is moved toward the edge of the discharge ( $N \sim 6 \times 10^7 \text{ cm}^{-3}$ ).



**Figure 4. Radial profile of the discharge source.**

Since the discharge is cylindrically symmetric, a radial density profile can be calculated from the lateral data using Abel's inversion. Figure 4 shows the radial profile of the discharge.

The time profile of the discharge is shown in Figure 5. The figure shows the number density of  $N_2^+$  as a function of time delay from the start of the discharge. Besides the dip around 150  $\mu$ s, the number density decreases gradually with time from its initial value around  $1 \times 10^8 \text{ cm}^{-3}$ .



**Figure 5. Time profile.**

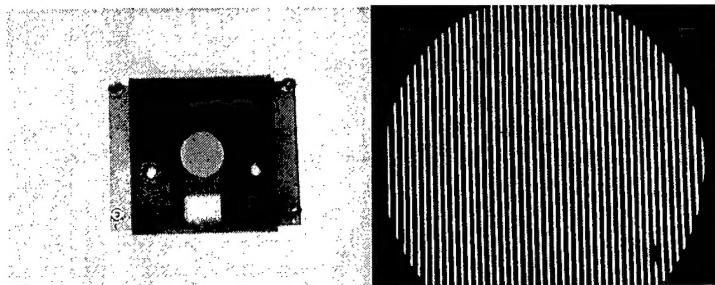
## B. HT-TOFMS

### Improved method for production of ion beam modulation devices

In HT-TOFMS, a continuous ion beam is sampled rapidly following a pseudo-random sequence of “on” and “off” pulses applied just prior to the flight chamber. The on/off modulation creates ion packets of various sizes, which interpenetrate one another as they drift through the flight tube. The detected signal is a convolution of the mass spectra corresponding to these packets. Using knowledge of the applied pseudo-random sequence, this signal is deconvoluted to yield a single mass spectrum.

To modulate the beam (deliver the sequence to the ion beam), we use an interleaved comb of wires called a Bradbury-Nielson Gate (BNG). A BNG consists of two electrically isolated sets of equally spaced wires that are in the same plane and

alternate in potential. When no potential is applied to the wires relative to the energy of the charged particles, the trajectory of the charged particle beam is non-deflected by the gate. In order to deflect the beam, bias potentials of equal magnitude and opposite polarity are applied to the two individual wire sets. Attraction to the negatively biased wires and repulsion from the positively biased wires cause ions to be deflected off the axis of their initial trajectory and to miss the ion detector.



**Figure 6. Bradbury-Nielson Gate with 100 micron wire spacing produced using our new winding procedure. The photo on the right side shows a 4.5 mm section of the gate viewed under a microscope.**

The strength and size of the BNG's effective field are related to the spacing between wires. Ideally the width of the modulation field in the direction parallel to the flight path would equal the diameter of the wires composing the gate.

In this case, the fate of an ion would be determined as it crossed the plane of the gate. In actuality, the effective field produced by a Bradbury–Nielson gate extends along the normal to the plane of the gate a distance on the order of  $0.80d$ , where  $d$  is the spacing between adjacent wires.

Finer spacing between adjacent wires allows better time resolution when gating or modulating the ion beam because of the corresponding decrease in the longitudinal extension of the deflection field perpendicular to the plane of the gate. Given that in TOF experiments the flight time is proportional to the square root of an ion's mass-to-charge ratio, this temporal resolution translates to the mass resolution of a TOF mass spectrometer. In the special case of HT-TOFMS, the validity of the deconvolution also

depends on the temporal accuracy of the modulation. In the past, our group was able to construct Bradbury–Nielson gates with wire spacing down to 160 microns, working by hand under a microscope to set the wires in a silicon-etched frame. This procedure was extremely laborious, requiring several days to complete, and yielded fragile BNGs with inconsistent quality.

Seeking to improve the quality of the gates and reduce the wire spacing, we developed a new method that allows production of Bradbury–Nielson gates with wire spacing as small as 0.075 mm, which can be constructed in three hours and which is readily adjustable. Moreover, our method is easily automated and the BNGs produced are consistent and robust. Instead of using etched silicon, we use synthetic polymers with a controlled groove spacing and profile. The grooves are produced using a machining process. Our greatly improved speed of assembly is achieved by using a hand-cranked weaving tool that feeds one continuous wire into the grooves. The alternating positive and negative sets of wires are wound separately and attached to electrically isolated contacts on the frame using epoxy adhesive. Figure 4 displays photos of a completed BNG produced by the new method and which is already adapted for use in our new modulation electronics; the spacing between wires is 100 microns. Individual BNGs have been used for over 6 months without complication of degradation. We have recently submitted a paper<sup>i</sup> detailing improvements in the performance of HT-TOFMS that resulted from the decrease in wire spacing. We expect that these finely spaced gates will lead to advances in other forms of TOFMS as well.

#### **Reconstruction of the HT-TOFMS: Second generation instrument**

In response to the effects of skewed modulation sequences detailed above, much of the last year was dedicated to the reconstruction of an instrument with optimized electronics.

The second generation HT-TOFMS can be equipped with a gas sampling glow discharge source (GSDS) or an electrospray ionization source (ESI). The instrument includes 4 differential pumping stages. The pressure in these stages is controlled by three turbo pumps, each of which is backed by mechanical pumps.

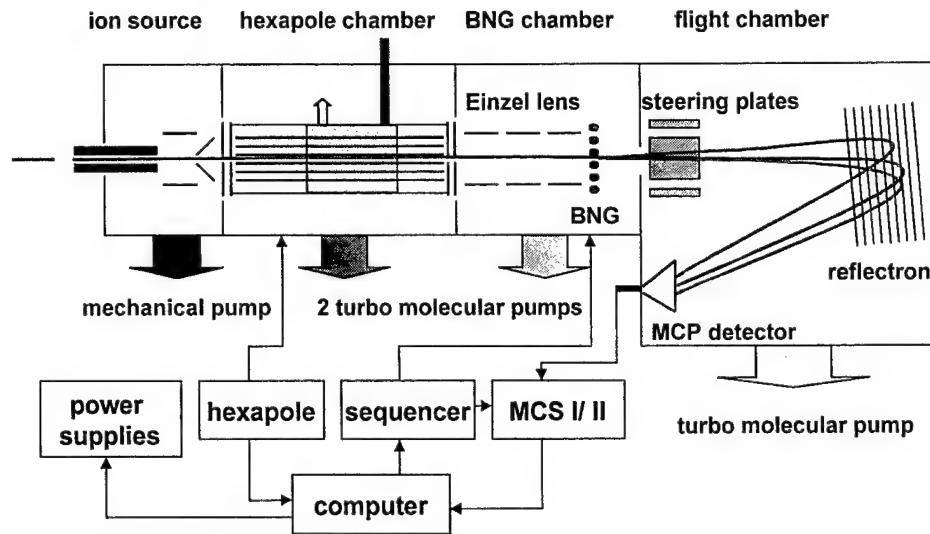


Figure 7. Experimental setup of the HT-TOFMS.

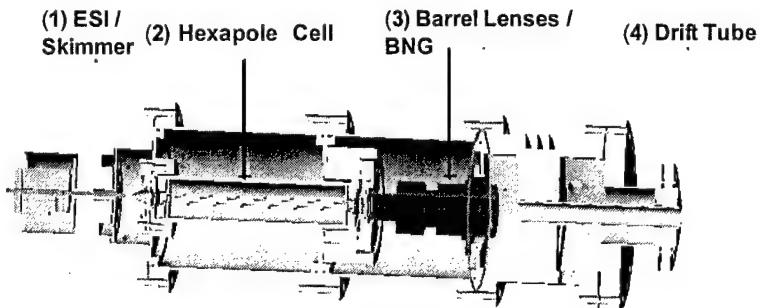


Figure 8. HT-TOFMS Instrument. The numbers correspond to the four differential pumping stages. Only the beginning of the drift tube is shown.

The ionization source, which can be used for gas sampling glow discharge and electrospray ionization experiments, is housed in a custom aluminum vacuum chamber that was designed and machined in our lab.

In the electrospray mode the source may be used with sheath-flow or sheathless electrospray emitters. Ions are sprayed into the front of a heated glass capillary, which

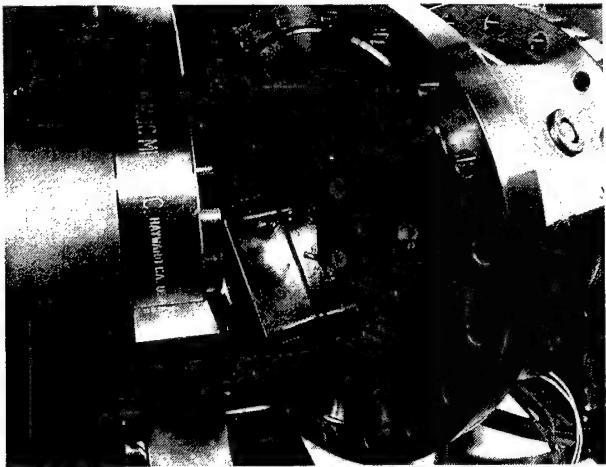
extends from atmospheric pressure into the instrument's first vacuum stage (pressure tunable between 500 mTorr and atmospheric pressure). The glass capillary has isolated, metal-coated ends; acceleration between the two ends of the capillary assists in declustering and desolvation of analyte ions to reduce the number of cluster peaks in our spectra. Cluster peaks have special significance in HT-TOFMS because the multiplexing advantage is maximized when spectra have fewer peaks. Declustering will be accomplished by balancing the effects of acceleration voltages, applied heat, and a counter gas flow. From this first vacuum stage, ions pass through a skimmer and a conductance-limiting lens into the second vacuum stage. Voltages between the heated capillary and the skimmer can be tuned to induce fragmentation of analyte ions.

The second vacuum stage is a stainless steel cylinder housing an rf-only hexapole. The combination of pressure and electric field within this cell is intended to induce collisional cooling of the ion beam prior to time-of-flight measurements. The pressure of the cell is a balance of three parameters: vacuum pumping, the jet stream entering the cell, and the flow of a collision gas (nitrogen, helium, or air). The instrument was constructed so that both pumping and the flow of collision gas are tunable.

Two of the primary factors governing resolution in all TOFMS instruments are ion kinetic energy distribution and the temporal/spatial duration of ion pulse. As TOFMS has evolved into the widely used technique that it is today, many tools have been developed to control these parameters. While HT-TOFMS is able to use a reflectron to correct for slight energy disparities, its on-axis modulation scheme and the rapid, pseudo-random modulation prevents us from implementing the often used technique of orthogonal extraction. We must, therefore, find other ways to dampening the energy given to ions during the ionization process. The supersonic jet expansion of the ion beam into vacuum yields ion kinetic energies spreads covering up to three orders of magnitude,

depending on the mass of the ions. In an effort to completely eliminate this kinetic energy spread, and, hence, ensure that the applied acceleration potential is the only determinant of flight times, we have installed an rf-only hexapole (cf. Figure 8 [2]) similar to that described by the groups of Douglas, Standing, and Hieftje. This device consists of a hexapole run without the varying dc component (so it is not a narrow range mass filter), operating in a cell containing a collision gas at a relatively high pressure (100 mTorr). Motion of ions through the hexapole is constrained to the central axis by the rf field, and collisions with gas molecules cause losses in energy. All of these groups have demonstrated significant improvements in sensitivity and mass resolution with the addition of such a device.

Ions exit the hexapole and enter the third differential pumping stage through two stainless steel lenses, which focus the beam and limit conductance. The third stage houses a set of three barrel lenses that focus the ion beam onto the beam modulation device for Hadamard encoding and consists of the Bradbury-Nielson Gate (BNG) and the modulation electronics (cf. Figure 9).



**Figure 9. Aluminum BNG vacuum chamber with heat sinking capabilities and installed modulation electronics and BNG.**

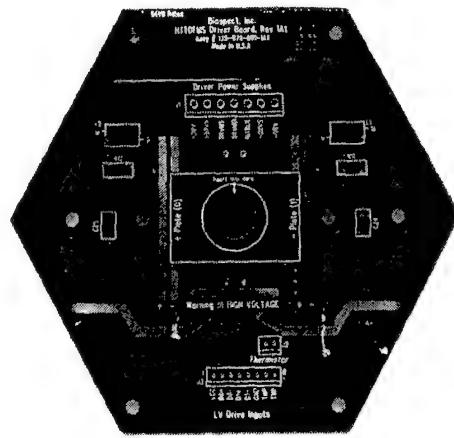
Special consideration was taken to dissipate the heat generated by the application of the high frequency sequence. The BNG is mounted in a custom aluminum chamber, which serves as a heat sink (Figure 9). The length and rate (up to 50 MHz) of these sequences (up to 16 bit), as well as the modulation voltages, are controlled from a PC. Sequences are generated by a series of shift registers.

The pulses of ions created at the gate pass into the field free drift tube, which is the final pumping stage. The total flight path of the ions from the BNG to the detector is 2.2 meter. The flight tube includes a reflectron that partially corrects for kinetic energy disparities in the ion packets. Ions are detected at a multichannel plate. The signal from this detector is amplified, and sent to the discriminator of a 2 GHz time-to-digital converter. Sequence timing and synchronization of the modulation and detection are controlled in a HT-TOFMS control system.

The instrument was designed for ultimate experimental flexibility. For example: all lens dimensions are adjustable, all pressures and voltages are tunable, custom (non-Hadamard) encoding sequences can be implemented from the PC, and each of the major components is housed in its own 8-inch conflat chamber, making it possible to easily remove, replace, or insert components.

## Accommodation of custom sequencer and integrated BNG / driver board

The majority of the sequence distortion was caused by electronic ringing in the amplified sequence. Ringing is a common problem in rf circuitry, which appears when the impedances within a network are poorly matched. In the case of HT-TOFMS, the ringing arose because of poor impedance matching between the driver circuitry (which amplifies the sequence to the modulation voltage), the BNG, and the transmission line connecting these two devices. Initially, we attempted to correct the problem by installing snubber circuitry designed to filter the ringing. It was eventually decided that the best approach would be to remove the transmission line and make the BNG and driver one unit.



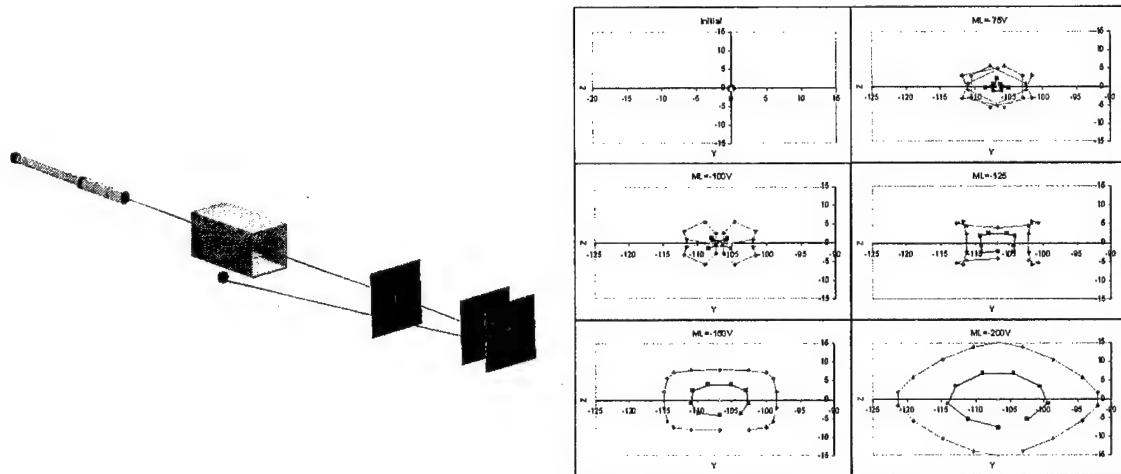
**Figure 10. Custom BNG/driver board without BNG. This device is mounted in vacuum with the BNG in order to eliminate ringing caused by the transmission line.**

The two primary concerns during design were space for the circuitry and dissipation of heat generated by the electronics in vacuum. We have since designed and installed an aluminum vacuum chamber that takes into consideration: the need to mount the electronics in vacuum, dimensions necessary to house all components and electronic leads, thermal conductivity of potential alloys, maximum heat dissipating metal, various cooling options (air, water, dry ice, immersion coolers, Peltier element...), compatibility with existing chambers, and access to the electronics for maintenance.

Simultaneous to the development of the integrated driver/BNG, the electronics generating the encoding sequence were redesigned. The new electronics are run from a

PC, and drive the two wire sets individually. With this sequencer, it is possible to apply custom and non-symmetric sequences to the wire sets. This feature greatly increases our capabilities to characterize and optimize the beam modulation process.

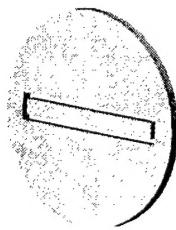
We are currently characterizing the improved electronics with the glow discharge source using air, nitrogen, argon, krypton, acetone and toluene as analytes to optimize the ion optics of the HT TOF mass spectrometer. All experimental results are compared to Simion models of the instrument, which begin with the high-pressure hexapole cell and include all subsequent optics (Figure 11).



**Figure 11. Schematic of instrument and examples of calculated beam cross sections.**

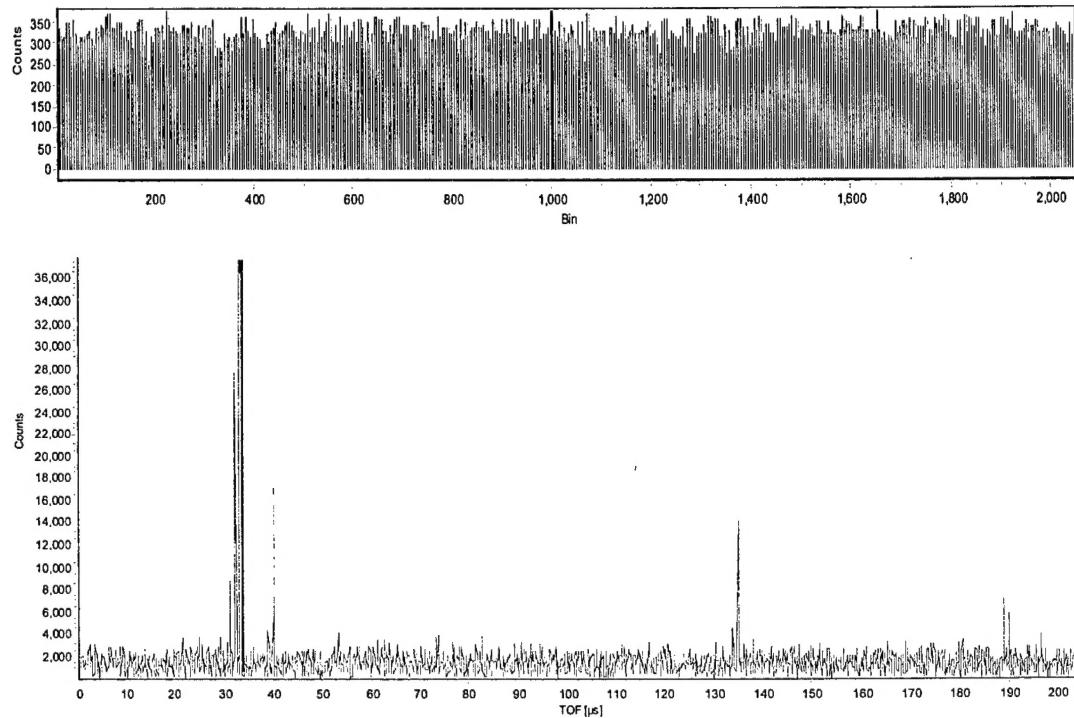
### 100% duty cycle experiment

Although obtaining a 50% duty cycle is a big step toward high-efficiency TOF mass spectrometry, this advantage can be pursued even further. Using a position-sensitive ion detector that is able to sense both the deflected and undeflected beams in different zones of its active area, we can attain a 100% duty cycle. This setup allows us to use of a Hadamard matrix instead of a Simplex matrix in the convolution process, thus increasing the SNR by 40%. This gain increase the spectral storage rate of the MS.

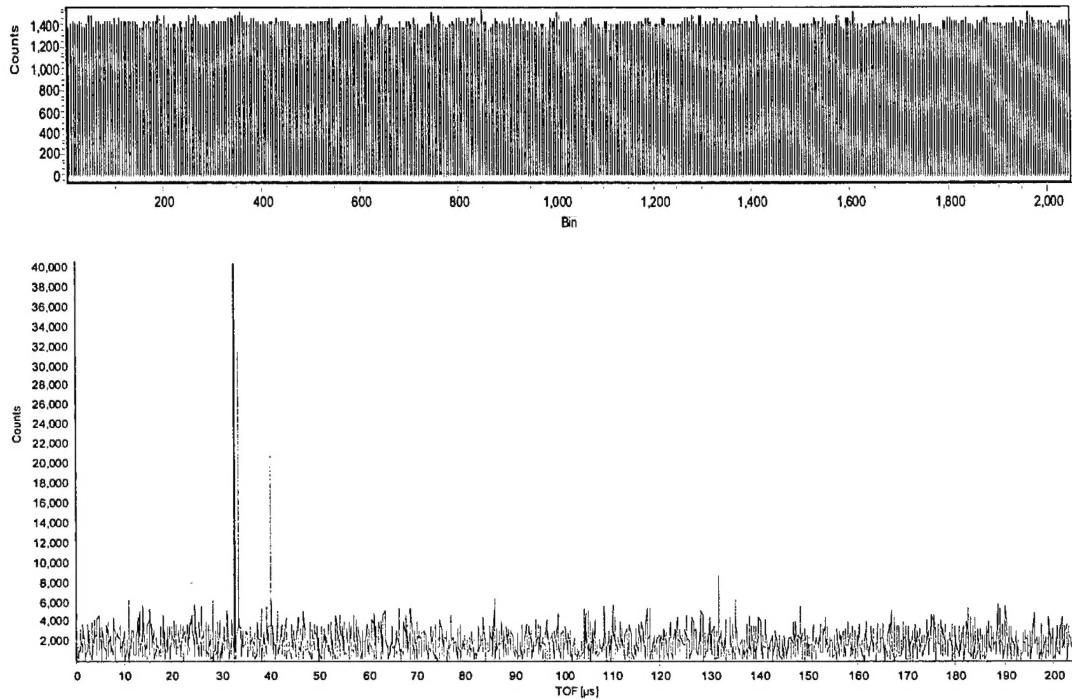


**Figure 12. Dual-anode MCP for detecting both modes of the modulated ion beam.**

Although fully position-sensitive ion detectors based on resistive anode encoders are already available, high-resolution (x,y) information is not necessary for implementing a full Hadamard encoding. Instead, a conventional MCP detector assembly with a two-zone patterned anode is used in the new design. A schematic of this device is shown in Figure 12. Such a dual-anode MCP, with dimensions based on beam profiles acquired with a 100- $\mu\text{m}$  BNG, was made for us by Quantar Technologies in Santa Cruz, CA.



**Figure 13. Glow discharge of air: Inner MCP. 11-bit Hadamard encoding, 10MHz modulation, 10MHz acquisition. Top: Raw spectrum, bottom: Deconvoluted spectrum.**



**Figure 14. Glow discharge of air: Outer MCP. 11-bit Hadamard encoding, 10MHz modulation, 10MHz acquisition. Top: Raw spectrum, bottom: Deconvoluted spectrum.**

Experiments demonstrating this MCP's performance have been carried out. Preliminary results obtained with the glow discharge source are depicted in Figure 13 and 14.

#### 4. PERSONNEL SUPPORTED

Richard N. Zare, Principal Investigator

Facundo M. Fernández, Postdoctoral Research Associate

Jose M. Vadillo, Postdoctoral Research Associate

Oliver Trapp, Postdoctoral Research Associate

Jonathan E. Flad, Graduate Student

Joel R. Kimmel, Graduate Student

Ignacio Zuleta, Graduate Student

Oh Kyu Yoon, Graduate Student

## **5. PUBLICATIONS**

None since last progress report

## **6. INTERACTONS/TRANSITIONS**

### **A. Participation/presentations at conferences:**

None

### **B. Consultative and advisory functions:**

None

### **C. Transitions:**

None

## **7. NEW DISCOVERIES, INVENTIONS, AND PATENT DISCLOSURES:**

None

## **8. HONORS/AWARDS**

Professor Richard N. Zare:

Hoagland Prize for Excellence in Undergraduate Education, Stanford University, 2003

Distinguished Chemist Award, American Chemical Society, Sierra Nevada Section,  
2002

Faraday Medal and Lectureship, Royal Society of Chemistry, 2001

Charles Lathrop Parsons Award, American Chemical Society, 2001

Nobel Laureate Signature Award for Graduate Education, American Chemical Society,  
2000

The Welch Award in Chemistry, 1999

Distinguished Service Award, National Science Board, 1998

California Scientist of the Year, 1997

National Medal of Science, 1983

Honorary degrees from:

Université Paul Sabatier, 2003

Hunan University, 2002

The University of York, 2001

State University of West Georgia, 2001

Uppsala University, 2000

Columbia University, 1999

Eidgenössische Technische Hochschule, 1993

Northwestern University, 1993

University of Arizona, 1990